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(71) Applicant: AGFA-GEVAERT naamloze  
vennootschap  
Septestraat 27  
B-2640 Mortsel(BE)

(72) Inventor: Tavernier, Serge Martin  
Bouwenstraat 40  
B-2547 Lint(BE)  
Inventor: Märksch, Paul  
Nikkelstraat 18  
B-2060 Antwerpen(BE)  
Inventor: Mampaey, Jozef Leonard  
Keizershoek 179C  
B-2550 Kontich(BE)  
Inventor: Zwijsen, Jan Albert  
Elzenhoutstraat 16  
B-2610 Wilrijk(BE)  
Inventor: Claes, Jan Freddy  
Van Dijkstraat 76  
B-2640 Mortsel(BE)  
Inventor: Janssens, Robert  
Asterstraat 22  
B-2440 Geel(BE)

(54) Color electrostatographic apparatus and method comprising intermediate fixing steps.

(57) An electrostatographic imaging process and apparatus is described wherein a multi color image is formed by the transfer to a receiver of a set of colored toner compositions and fixing of the entire set of colored toner compositions transferred to said receiver characterised in that at least once and according to a preferred mode, after each transfer to said receiver of a colored toner composition and before the transfer to said receiver of the subsequent colored toner composition, a sintering of the transferred colored toner composition unto said receiver is executed. The electrostatographic imaging process may either be a xerocopying or xeroprinting process, whilst the sintering is preferentially executed by the application of the flash fusing process, e.g. by a Xenon flash lamp, and the final fixing is preferentially executed by the application of the heated

roller fusing process.

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## Field of the invention

The present invention relates to electrostatography and more in particular to an electrostatographic method and apparatus for the production of color images.

## Background art

The electrostatographic process and image-forming apparatus for the application of this process are widespread nowadays and well known to those skilled in the art.

Particular aspects hereof are set forth in R.M.Schaffert "Electrophotography", the Focal Press, London, New York, enlarged and revised edition, 1975, as well as in numerous patent specifications.

The most widespread application of the electrophotographic process is the production of medium-quality black and white copies of an original. In this process a latent electrostatic charge pattern is formed on a photoconductive dielectric element, which is subsequently developed by a one or two component developer composition, the toner image is then transferred to a receiver such as paper or a transparent thermoplastic sheet material made of e.g. polyethylene terephthalate, and fixed unto said receiver by one of the numerous fusing methods, e.g. the heated roller fusing process.

Recently considerable development efforts have been made for the production of colored images by the electrophotographic process.

Most efforts have been directed to the development of xerographic processes and apparatus for the production of a relatively low number of medium quality color copies of various originals.

In conventional electrophotographic color systems, toner or developing particles of at least three different colors are employed to make up any desired full color image. Colored image formation should however not be limited to electrophotographic systems alone as any electrostatographic system offers equal possibilities. Generally, at least three color separation images are formed and the combined images registered with each other to form the color reproduction of the full color original.

When in particular the xerotyping process is applied in a color electrostatographic apparatus, at least three masterplates are formed by exposure in contact with at least three different optical separation images. The electrostatographic image on each of the masterplates is then developed with a different color toner, and subsequently the toner images are combined to form the final full color image. This combination of the color toner images is generally made on a final receiver sheet such as

paper to which the toner images are permanently affixed.

In the prior art color electrostatographic systems, also in those systems aiming at higher image quality, the receiver carrying the colored developer compositions is processed at the end of the entire processing cycle in order to fuse the image to the receiver. EU-A-0 376 732 discloses color-image forming apparatus adopting the multi-color electrophotographic systems. In all embodiments disclosed in said application, the full-color toner image lying on the receiver is only fixed at the end of the processing cycle. The main reasons for fusing the full color image at the end of the processing cycle arise from the lack of dimensional stability of the receiver for common fusing procedures, inducing a misfit for registration when any conventional intercolor-fusing would be applied. When no intermediate fusing takes place the following problem arises: the image formed by the colored toner particles onto the receiver is disturbed during the further processing and transport of said receiver through the color electrostatographic apparatus, and is particularly disturbed during subsequent transfer steps of subsequent colored toner particles from the image bearing member(s) to the receiver.

Said disturbance includes the partial pick-up of previously deposited toner particles from the receiver to the image bearing member during subsequent toner transfer steps, the latter phenomenon giving rise to a loss of density of the corresponding color, and color-misfit in the final color image.

Moreover this phenomenon, called "retro-toner-pick-up" is dependent on the presence or absence of the subsequent colored toner layer: the pick-up is more pronounced when a bare or naked image bearing member contacts the previously deposited toner layer(s) in comparison to the situation where a toned image bearing member contacts some previously applied toner layers on the receiver. This phenomenon induces by this process an image-dependent retro-toner-pick-up, giving rise to additional image quality degradation.

Another problem caused by the toner particles present on the receiver is the formation of an electrical counter potential on said receiver, hampering the transfer of toner particles to said receiver in the subsequent transfer stations. Said counter potential increases as a function of the amount of toner mass already present on said receiver following simple laws of electrostatics, related to capacitors.

The above mentioned problems could theoretically be solved by fusing the transferred toner particles on the receiver after each transfer of toner particles to said receiver. Therefor theoretically one of the common fusing methods as set forth hereinafter could be used.

Indeed, different types of fusing processes can be used for fusing a toner powder image to its support. Some are based upon fusing by way of softening the toner image by heat, others are based on softening by solvent vapours, or by the application of cold flow at high pressure in ambient conditions of temperature. Both cited fusing processes, not based on the application of heat, have typical draw-backs. Solvent vapour fusing or sintering will imply use of solvents with low vapor pressure, and good solvation properties towards the resin. Inflammation, and/or explosion risks and/or toxicological and ecological problems arise from solvents suited for such purpose. For example such solvents are found within the ketones, esters, or halogenated hydrocarbons. Cold pressure fusing implies deformation of receivers, commonly called calandering changing appreciably their final appearance, and implies some soft properties from toner which poses problems with respect to lifetime of corresponding developers. In the fusing processes based on heat, four major types should be considered. The first is an oven heating process in which heat is applied by hot air over a wide portion of the support sheet, the second is a flash heating process in which heat is produced in the toner by absorption of light energy emitted by a flash lamp, the third is a radiation process wherein the receiver with the toner image is irradiated mainly by infrared-radiation, and the fourth is a heating process wherein the support with the toner image is simultaneously pressed and heated. The latter process is commonly called the heated roller fusing process.

This first problem cited above (disturbance of color image on the receiver by retro-toner-pick-up) could be overcome by fusing the toner to the receiver. The Second (formation of an electrical counter potential) could be overcome by reducing the toner-viscosity so drastically during the fusing process that discharge occurs.

However the application of multiple fusing steps to one and the same receiver causes said receiver to lose its dimensional stability and consequently its color-registering. It also causes easy wrinkling of said receiver, which gives rise to numerous paperjams in day-to-day operation of the color electrostatographic apparatus.

#### Objects of the invention

It is an object of the present invention to provide an electrostatographic apparatus and process for the production of high quality color images.

It is a further object of the present invention to provide an electrostatographic apparatus and process for solving the abovementioned problems.

Other objects and advantages of the present

invention will become clear from the following description.

#### Summary of the invention

We now have found that the problems mentioned above resulting from the sole fusing of the full set of colored toner images on the receiver after performance of the entire color processing cycle, may be solved by applying a partial, intermediate, fusing after each transfer of toner particles to the receiver. Hereinafter this weak form of fusing will be called a sintering process, being an intermediate fusing causing a softening of the toner particles transferred to said receiver, said softening giving rise to a light sticking of said particles to each other as well as to said receiver, and to a partial decay of the countertension built up by said particles. The sintering process gives rise only to a very weakly fused layer of toner particles, as becomes apparent by applying a rubbing test on said layer: nearly all toner is easily removed from the receiver.

It is of prime importance to realise this sintering process (for n-colors it should be performed n-times) in such a way as to conserve the dimensional stability of the receiver in order to conserve appropriate registration of the various colored toner-images deposited on the receiver.

Therefore, in accordance with the present invention, there is provided an imaging process and apparatus wherein a multi color image is formed by the transfer to a receiver of a set of colored toner compositions and fixing of the entire set of colored toner compositions transferred to said receiver characterised in that before said fusing at least once a partial fixing called sintering of (a) transferred colored toner composition(s) to said receiver is executed. According to a preferred mode of our invention, said sintering is executed after each transfer to the receiver of a colored toner composition.

According to a further preferred embodiment of our invention, the sintering is based on the application of the flash fusing process whereby the radiation energy is preferentially absorbed by the developer particles, not by the receiver.

According to a further preferred embodiment, a Xenon or Krypton flash bulb is used in said flash fusing station.

According to a further preferred mode, whereas the intermediate fusing stations are flash-fusing stations, the final fusing of the full color image on the receiver is effected in a heated roller fusing system.

According to a further preferred embodiment, said set of colored developer compositions is a set of blue, red and green developer compositions or a

set of cyan, magenta, yellow and black developer compositions.

According to a further preferred embodiment said sintering is performed, by applying the flash energy on the toner image bearing receiver, the latter being in contact with a cold backing member, so as to allow sufficient heat loss in order to maintain the toner bearing receiver at ambient temperature.

#### Detailed description of the invention

##### Xerocopying - Xeroprinting applications

The apparatus and method of our invention is suitable for the production of full color images according to either the xeroprinting process, or the xerocopying process. The essential difference between the conventional electrophotographic (i.e. xerocopying) process and the xeroprinting process resides in the fact that in the latter process a masterplate comprising e.g. a photopolymerisable composition coated on a grounded conductive receiver is used as image bearing member, instead of a photoconductive drum, as is the case in the xerocopying process. The latent image in case of xeroprinting consequently is a persistent image. As a consequence hereof, xeroprinting is particularly suitable for the production of short run (color) copies of the same original.

Particulars of the xeroprinting process may be found in the article entitled "Electrostatic Image Forming by using Photopolymerizable Monomers" from E. Inoue and H. Fukutomi, published in the Journal of the Society for Photographic Science and Technics, Japan 4 1 (1978) No. 5, pages 333 to 340; in EU A 0 243 934 or in EP A 89202664.2.

The present invention will now be described hereinafter and illustrated by means of the accompanying figures focussing on a xeroprinting and xerocopying process.

Figure 1 is a schematic cross-sectional representation of an apparatus according to our invention suitable for the application of the xeroprinting process.

Figure 2 is a schematic cross-sectional representation of an alternative embodiment of the apparatus of figure 1, wherein the receiver is transported on an endless belt.

Figure 3 is a schematic cross-sectional representation of a xerocopying apparatus incorporating the teachings of our invention.

It is obvious, however, that the invention does not limit itself to the type of processes and apparatus cited above, but comprises electrostatographic, ionographic, and electrophotographic processes as well. The term 'electrostatographic' as used herein

should be interpreted as encompassing ionographic and electrophotographic processes as well.

Further Figure 4 shows a typical emission spectrum of a Xenon flash lamp.

Figure 5 shows the absorbance spectrum of white paper.

Figure 6 shows the absorbance spectrum of a black colored toner composition.

Figures 7, 8 and 9 show the absorbance spectrum of a typical magenta, yellow and cyan colored toner composition.

Application of the invention in a xeroprinting apparatus and process.

The xeroprinting imaging process essentially comprises the following steps: illumination of the masterplate and attachment of said plate to the drum, charging of said plate to produce a latent image of electrostatic charge, developing said latent image by toning, and finally transferring the toner image by electrostatic or other means to the receiver.

Since the practice of xeroprinting is well known to those skilled in the art, the various processing stations are represented in Fig. 1 as blocks and a brief description will hereinafter be given for the purpose of illustrating the general operation of a xeroprinting apparatus which can embody the teachings of the present invention. With respect to the registering of the set of colored developer compositions to be transferred to the receiver, reference is made to a co-pending application, filed on even date herewith entitled "A process and apparatus for the production of colour images".

Overall description of the xeroprinting process and apparatus.

As is apparent from Figure 1, the electrostatographic apparatus of our invention comprises at least three and preferably four stations (numbered A, B, C and D). In each station a colored toner composition (e.g. red, green or blue, or yellow, cyan and magenta, and preferably also black colored toner composition) is image-wise transferred to a receiver. These stations are to a large extent identical; the description hereafter will explain in detail the performance of station A with reference to the appropriate parts of station A in figure 1.

A drum like member 11, comprising a master as described hereinafter moves along a charging station 12 by rotation by means of a shaft 13.

##### Charging

A uniform electrostatic charge is placed over the master plate on the drum 11, e.g. by a corona generating device comprised within said charging station 12. Apart from a simple corona discharge, a

more complex charging unit such as a scorotron may also be used.

#### Development

Thereafter the rotation of the drum causes the master plate carrying the recorded electrostatic latent image to pass through a development station 14, using e.g. magnetic brush development. In said magnetic brush development system the recorded electrostatic latent image is developed by bringing it into contact with a brush of developer mix, brought about by applying a directional flux field to a magnetizable developer mix of carrier granules and toner. Apart from magnetic brush development, other development processes such as e.g. cascade development, touch-down development and other powder cloud development are also suitable. The colored developer composition used in the development station is described hereinafter in detail.

#### Transfer and cleaning station

After development, the toner image is transferred in a transfer station 15, e.g. by transfer corona's 16, from the master to the contacting side of a sheet of final Receiver 17 such as plain paper, labels, or transparencies, as desired. The transfer of the electrostatically deposited colored toner composition may also proceed e.g. by applying a sufficient voltage (e.g. 3 kV) to a conductive roller, e.a. metal roll, which is kept in close ohmic contact with the rear side of a paper sheet acting as receiving material whose front side is therefore kept in close contact with the toner image on the drum like member 11.

The sheet of Receiver 17 may be provided by a transport roller pair 18 and may be supplied to said transport roller pair by conventional sheet dispensing devices 19 wherein each sheet is caused to slide off a stack of sheets by use of feed rollers or sucker-cups or by peeling action.

Invariably, although a preponderance of the toner powder is separated from the master surface of the drum-like member 11 by transfer to the final sheet of Receiver 17, some residual toner particles remain thereto. These particles are cleaned from the master surface at cleaning station 20. At said cleaning station the residual toner particles are first brought under the influence of a cleaning corona generating device 21 adapted to neutralize the electrostatic charge remaining on the toner particles. The neutralized toner particles may then be cleaned from the master surface by conventional mechanical means 22 as for example the use of mechanical brushes, a web, or cleaning blade.

The master surface may then be used for the

next successive imaging cycle.

Thereupon the sheet carrying the toner image is advanced e.g. by a belt transport mechanism 23 through the intermediate fusing station 24 to provisionally sinter the toner image on said Receiver.

#### Intermediate fusing station

In figure 1 the Receiver 17 bearing a toner image on its upper surface is seen passing through the first intermediate fusing station 24, which comprises basically two parts.

The portion of the fusing station 24 above Receiver 17 is made of a housing comprising a radiant source of energy 25 mounted in a reflector cavity. A shield for the lamp, such as a quartz shield, that is substantially transparent to the radiation, may be provided to shield the lamp and the reflector means from the Receiver, debris and other machine impurities.

According to a preferred embodiment, the lamp is a Xenon flash bulb, such as the Xenon flash type QG 8902 AGIV/2, available from Heimann AG, Wiesbaden, Germany. Said lamp should preferably be mounted in a polished aluminium housing, and be provided with an electronic discharge circuit enabling a typical discharge time in the range from 0.01- 100 msec, more preferably 0.1-10 msec. The energy irradiated onto the receiver carrying the toner image then is situated between 0.1 and 0.5 J/cm<sup>2</sup>. A typical spectrum of such lamp is shown in figure 4. (Spectral irradiance, expressed in % vs wavelength expressed in nm).

The portion of the fusing station 24 below Receiver 17 may comprise a belt transport mechanism 23 as shown in figure 1 or may comprise a roller for guiding and supporting the sheet of Receiver 17 through the fusing station 24. Said roller should then be characterised by the fact that its outer surface, contacting the sheet of Receiver 17, moves synchronously with the speed of advancement of said sheet of Receiver through the entire apparatus. It is an advantage to make during the sintering process a back-contact between the toner bearing receiver and a cold backing member or component thereof, allowing good heat dissipation from the receiver to that component, resulting in a non-heated situation for the receiver.

Therefore, it has been found that sintering induced by irradiation of the several toners on the receiver with appropriate radiation with regard to spectrum and intensity offers the possibility to heat preferentially the toners, affecting only marginally the receiver.

Moreover if the receiver covered with toner is back contacted with a back-electrode, as described above, heat dissipation, if present in the receiver, can be realised readily, dimensional stability is

realised without any problem.

Very interesting irradiation spectrums with respect to toner absorbances for yellow, cyan, magenta and black toner without affecting receivers are found when applying the flash fusing process. A typical emission spectrum for a xenon flash bulb is set forth in fig. 4. As is apparent from fig. 5 the absorbance spectrum of white paper shows the quasi impossibility to capture any energy from the cited reference spectrum. The absorbance spectrum of a particular magenta colored developer composition, comprising Permanent-Carmin FBB available from Hoechst, is shown in fig. 7, the absorbance spectrum of a typical yellow colored developer composition, comprising Sico-Echtgelb D 1355, available from BASF, is shown in fig. 8, the absorbance spectrum of a typical cyan colored developer composition, comprising Cuphalocyanine is shown in fig. 9, while the absorbance spectrum of a typical black colored developer composition comprising carbon black is shown in fig. 6. In the figures 6 to 9, the absorbance spectra are set forth expressed in % in ordinate vs the wavelength, expressed in nm. From the comparison of the emission spectrum of the Xenon flash bulb, it is clear that the use of such Xenon flash fusing system is ideally suited for selectively fusing or sintering the toner internally and to the paper receiver without heating up the receiver itself. This results in a high dimensional stability of the receiver in spite of the multiple intermediate fusing or sintering steps.

After a first colored toner composition has been transferred and sintered unto the receiver 17, said receiver passes through subsequent modules or stations of the color electrostatographic apparatus according to our invention. In said subsequent modules, subsequent colored toner compositions are transferred and sintered and partially fused to the receiver. The support 17 may be transported through the entire color-imaging apparatus by means of roller pairs 18, or a combination of roller pairs 18 and belt mechanisms 23, or by means of an entire feeding belt successively passing the respective color-transfer stations and intermediate fusing stations 24, 34 and 44. Such entire feeding belt is disclosed i.a. in the cited EU-A-0 376 732 or in our compending application filed on even date herewith.

#### Final fusing station

After the receiver 17 has passed the last module of the apparatus of our invention for the transfer of the last colored developer composition to said receiver, a final fusing of the entire set of colored developer compositions to said receiver should take place. For said final fixing, a heat- and pres-

sure fusing process is preferentially used.

In a common heat- and pressure fusing process the support carrying the non-fixed toner image is conveyed through the nip formed by a heating roller also called fuser roller 51 and another roller backing the support and functioning as pressure exerting roller, called pressure roller 52. This roller may be heated to some extent so as to avoid strong heat loss within the copy.

This fusing process is preferentially employed as final fusing process in the apparatus resp. method according to our invention since a remarkably high thermal efficiency is obtained because the surface of the heating roller is pressed against the toner image surface of the sheet to be fixed. Further, since the energy acceptance is independent from the wavelength, the entire set of colored toner compositions is evenly fused. Moreover this fusing process allows double-sided copying, or so-called duplex printing.

The major and important drawback of this fusing process is the inherent danger of the occurrence of so-called offset-phenomena.

If the fuser roller provides too much thermal energy to the toner and paper, the toner will melt to a point where its melt cohesion and melt viscosity is so low that "splitting" can occur, and some of the toner is transferred to the fuser roller. When splitting does occur the toner which is taken up by the fuser roller is usually transferred to the copy sheet during the next turn of the roller, giving rise to the phenomenon of the so-called "hot offset", and this occurs in particular when there is inadequate release and/or (cleaning). Such release should be provided and is commonly provided by wetting the fuser roller directly or indirectly with silicone oil.

Too little thermal energy on the contrary results in poor adhesion of the toner to the paper resulting in poor fusing.

In this case the toner particles may fuse together and to the roller but they do not fix to the paper - especially since the thermal energy is delivered through the toner. The unfixed, fused toner particles will likewise be deposited onto the copy sheet during the next turn of the roller, resulting in what is called "cold offset".

In both cases, 'cold' as well as 'hot' offset, some toner will be transferred to the pressure roller during the lapse of time between subsequent paper feedings, giving additional contamination on the back of the copy.

In order to prevent as much as possible the above described toner offset and to achieve good fusing quality two kinds of measures are applied in the apparatus of our invention. First, the fuser roller 51 is coated with an abhesive material such as silicone rubber, or is provided with a smooth coat-

ing of polytetrafluoroethylene resin having a very low friction coefficient and low adhesivity. Secondly the fuser roller 51 is wetted with silicone oil directly or indirectly and a mechanical cleaning means is provided, namely a scraper blade.

Alternative embodiment of a xeroprinting apparatus embodying the teachings of our invention.

Figure 2 is a schematic cross sectional representation of a xeroprinting apparatus similar to the apparatus of fig. 1 described above; however the receiver is transferred throughout the entire apparatus by means of an endless belt. With respect to the various parts of this apparatus, reference is made to our copending application filed on even date herewith entitled 'A process and apparatus for the production of a colour image'. 75, 76 and 77 indicates the intermediate fusing stations according to our invention and 78 indicates the final heated roller fusing station, both as described above.

#### Overall description of the xerocopying method and apparatus

As set forth hereinabove, the apparatus and method of our invention are also suitable for being applied in a conventional electrophotographic system, i.e. a xerocopying system instead of a xeroprinting system. Figure 3 is a schematic cross-sectional representation of a xerocopying apparatus incorporating the teachings of our invention. As may be seen from this figure, said apparatus comprises the following parts :

- (91) a drum-like member, coated with a photoconductive layer;
- (92) a charging station;
- (93) an illumination means;
- (94) a development station;
- (95) a drum-like member, carrying the receiver whereupon the full color xerographic image is to be formed;
- (96) an intermediate fusing station;
- (97) a cleaning device.

The charging station (92), the intermediate fusing station (96) and the cleaning station (97) are essentially similar to the corresponding devices described in the xeroprinting apparatus hereinbefore and therefore will not be described in detail again. A similar embodiment of the color-xerocopying apparatus set forth above, is disclosed in the cited EU-A-0 376 732, reference fig. 4.

The drum-like member (91) may e.g. be an  $As_2Se_3$  coated conductive drum, commonly used in xerocopying devices, or a drum coated with an organic fotoreceptor such as disclosed e.g. in EU-A-0 347 960, EU-A-0 347 967, EU-A 0 349 034 or one of the numerous other patents in this field. Belt-like photoconductive members instead of drum-like members can also be envisaged. The

illumination of the photoconductive drum (91) may be effected through an optical system, as in a conventional copying system, whereby at least three, and preferentially four color separation film sheets consequently serve as original for the illumination of said drum. According to a preferred mode of operation, the illumination of the photoconductive drum is effected by a laser system or a light emitting diode system. Such system illuminates the drum according to an illumination pattern corresponding to an electronically available image in the form of digitized data stored in a computer memory. The separation of the full color original in three (or four) color separations is then performed by scanning the full color original by means of an electronic scanner; and electronically converting said full color original in three (or four) electronically available color separations.

The development station (94) comprises in total at least three, and preferentially four modules, each module acting as a development station of the type described supra for the xeroprinting apparatus for one particular colored developer composition. The entire development station (94) is automatically turned over a quarter of a circle, such that the electrostatic latent images formed on the photoconductive drum, corresponding to the color separations of the full color original are sequentially developed by the colored developer compositions contained in the developing modules of said development station (94).

After the transfer and partial sintering of the four colored developer compositions on the receiver, a final fusing of the entire set of colored developer compositions on said receiver is effected. According to a preferred mode, said final fusing is effected in a heated roller fusing system as described above.

From the description hereinabove it is clear that the apparatus and method as described according to figure 1 for the application of the xeroprinting process may mutatis mutandis also be used for the application of the xerocopying process and that the apparatus and method as described according to figure 3 for the application of the xerocopying process may mutatis mutandis also be used for the application of the xeroprinting process.

Illumination of the masterplate used in the xeroprinting apparatus

The illumination of the xeroprinting master plates to be attached to the drum-like member 11 shown in figure 1 may be effected by either analog or digital means. In case of analog exposure, a line or half-tone negative or pattern is interposed between the source of illumination and the plate. Dependent on the number of color separation films



used - at least three - three or more masterplates are illuminated and attached to the drum like members 11 of the various modules of the color electrostatographic apparatus of our invention. As the photopolymerizable system of the xeroprinting masterplate is most sensitive to shorter wavelength light, an UV light source is preferred for the illumination of said plate.

In case of digital exposure, a light-emitting device, such as a laser, scans the films in raster fashion corresponding to digitized data describing the electronically available image.

In both instances, illumination of the photopolymerizable film must be sufficiently intense so as to bring about a sufficient degree of polymerization in exposed areas and provide the required difference in conductivity between exposed and non-exposed areas.

Photopolymerizable master plate used in the xeroprinting apparatus

The photopolymerizable electrostatic master plates for use in the apparatus of our invention generally comprise an electrically conductive receiver, e.g. aluminized polyethylene terephthalate, whereupon a layer of photohardenable composition has been coated. The latter layer generally is made up of an organic polymeric binder, a monomer compound, polymerizable upon exposure to actinic radiation, a photoinitiator, sensitizers, stabilizers, as well as various other additives.

Examples of photohardenable compositions suitable for use in the apparatus of our invention are described in the Article of E. Inoue and H. Fukutomi, cited above, as well as in EU-A-0279960 and EU-A-892026642 already cited. Suitable examples of photoinitiators are e.g. free-radical producing oxime esters such as are disclosed in US P 3558309 of U.L.Laridon and G.A.Delzenne, issued January 26, 1971.

A protective coversheet is preferably laminated to the photopolymer surface.

Developers used in the xeroprinting or xerocopying apparatus

Various kinds of dry developers may be used for applying the present invention. When high resolution printing or proofing applications are envisaged, it is recommended to use very fine toner particles, corresponding to a well-defined particle size distribution. An example of such toner composition as well as its preparation is disclosed in e.g. EU-A-89201695.7. Colored developers suitable for use in our invention are either two-component or mono-component developer compositions. In case of two-component developers, the toner gen-

erally comprise a resin binder, a colorant, and one or more additives such as a charge control agent and a flow enhancing agent.

## 5 Resins

Illustrative examples of toner resins useful for being applied into the apparatus of our invention include numerous known suitable resins such as 10 polyesters, polymers of styrene/butadiene, styrene/methacrylate, styrene and acrylate, polyamides, epoxies, polyurethanes and vinyl resins. Suitable vinyl resins include homopolymers or copolymers of two or more vinyl monomers. Partic- 15 particularly suitable vinylic resins for use in toners suitable for use in the apparatus of our invention, as well as their mode of preparation, may be found in EU-A-0380813. A particularly suitable polyester resin is ATLAC T500 (trade name of Atlas Chemical Industries Inc., Wilmington, Del. USA) being a propoxylated bisphenol A fumarate polyester, and 20 discussed more in detail in EU-A-89 201 695.7.

## Pigment Particles

25 In respect of pigment particles, the colored toner compositions of the present invention may contain various known cyan pigments, magenta pigments, yellow pigments, red pigments, green pigments, or blue pigments, and mixtures thereof. 30 Illustrative examples of cyan pigments include copper tetra-4-(octadecylsulfonamido) phthalocyanine, the X-copper phthalocyanine pigments listed in the color index as CI 74160, CI Pigment Blue 15, an Anthradanthrene blue identified in the color index 35 as CI 61890, Special Blue X-2137 and the like; while illustrative examples of yellow pigments that may be selected include diarylide yellow 3,3-dichloro benzidine acetoacetanilide a monoazo pigment identified in the color index as CI 12700, CI 40 Solvent Yellow 16, a nitrophenyl amine sulfonamide identified in the color index as Foron Yellow SE/GLF, CI Dispersed Yellow 33, 2,5-dimethoxy-4-sulfonoanilide phenylazo-4-chloro 2,5-dimethoxy 45 acetoacetanilide, permanent yellow FGL, and the like. Illustrative examples of magenta materials that may be selected as pigments, include for example 2,9-dimethyl substituted quinacridone and anthraquinone dye identified in the color index as CI 60710, CI Dispersed Red 15, a diazo dye identified 50 in the color index as CI 26050, CI Solvent Red 19, and the like. Apart from pigments, soluble coloring agents may be used as well.

## 55 Flow enhancing additives

In order to improve the flow properties of the developer compositions used in the apparatus of



our invention the toner particles may be admixed with flow enhancing additives. These additives mostly are extremely fine inorganic or organic materials. Widely used in this context are fumed inorganics such as silica, alumina or zirconium oxide or titanium oxide. The use of silica as flow improving agent for toner compositions is described in the United Kingdom Patent Specification No. 1,438,110.

The fumed silica particles suitable for use in the toner composition for use in the apparatus of our invention have a substantially spherical surface and are preferably coated with a hydrophobic layer such as obtained by methylation. Their specific surface area is preferably in the range of 100 to 400 sq.m/g.

Fumed silica particles are commercially available under the Trade Marks AEROSIL and CAB-O-SIL marketed by Degussa, Frankfurt (M), W.Germany and Cabot Corp. Oxides Division, Boston, Mass., U.S.A. respectively. AEROSIL R972 is a fumed hydrophobic silica having a specific surface area of 110 sq.m/g. The specific surface area can be measured by a method described by Nelsen and Eggertsen in "Determination of Surface Area Adsorption Measurements by continuous Flow Method", Analytical Chemistry, Vol. 30, No. 8 (1958) 1387-1390.

The preferred proportions of fumed silica to toner material are in the range of 0.5 to 3 % by weight.

In addition to fumed silica, a metal soap e.g. zinc stearate as described e.g. in the United Kingdom Patent Specification No. 1,379,252, may also be used as additional flow improving agent. Other flow improving additives are based on fluoro-containing polymer particles of sub-micron size.

The preferred proportions of metal soap such as zinc stearate to toner material are in the range of 0.05 to 1 % by weight. Particularly suitable flow enhancing additives are disclosed in EU-A-90113845.3.

#### Charge control agent

To enhance the chargeability in either negative or positive direction of the toner particles (a) charge control agent(s) is (are) added to the toner particle composition as described e.g. in the published German patent application (DE-OS) 3,022,333 for yielding negatively chargeable toner particles or as described e.g. in the published German Patent application (DE-OS) 2,362,410 and the United States Patent Specifications 4,263,389 and 4,264,702 for yielding positively chargeable toner particles. A very useful charge control agent for offering positive charge polarity is BONTRON N04 (trade name of Oriental Chemical Industries -

Japan) being a resin acid modified nigrosine dye which may be used e.g. in an amount up to 5 % by weight with respect to the toner particle composition. A very useful charge control agent for offering negative charge polarity is BONTRON S36 (trade name of Oriental Chemical Industries - Japan) being a metal complex dye which may be used e.g. in an amount up to 5 % by weight with respect to the toner particle composition.

#### Preparation of toner

In the preparation of the toner the coloring material and other additives are added to the molten resin and are subjected to kneading until a homogeneous mixture is obtained. After cooling, the solid mass obtained is crushed and ground e.g. in a hammer mill followed by a jet-mill. After this operation, air classification is effected.

For a given charge density of the latent image charge-carrying surface the maximum development density attainable with toner particles of a given size is determined by the charge/toner particle mass ratio, which is determined substantially by the triboelectric charge obtained by friction contact with carrier particles in case of a two-component developer.

#### Carriers

In case a two-component colored developer composition is used in the apparatus of our invention, the toner composition should be used in combination with carrier particles.

Useful carrier materials for cascade development include sodium chloride, ammonium chloride, aluminium potassium chloride, Rochelle salt, sodium nitrate, aluminium nitrate, potassium chlorate, granular zircon, granular silicon, silica, methyl methacrylate, glass. Useful carrier materials for magnetic brush development include, steel, nickel, iron, ferrites, ferromagnetic materials, e.g. magnetite, whether or not coated with a polymer skin. Other suitable carrier particles include magnetic or magnetizable materials dispersed in powder form in a binder as described e.g. in US-P 4,600,675. Many of the foregoing and typical carriers are disclosed in U.S.Pat. Nos. 2,618,441; 2,638,416; 2,618,522; 3,591,503 and 3,533,835 directed to electrically conductive carrier coatings, and U.S.Pat. No. 3,526,533 directed to polymer coated carriers. Oxide coated iron powder carrier particles are described e.g. in U.S.Pat.No. 3,767,477. The U.S.Pat.No. 3,847,604 and 3,767,578 relate to carrier beads on the basis of nickel. An ultimate coated carrier particle diameter between about 30 microns to about 1000 microns is preferred. The carrier particles possess then sufficient inertia to

avoid adherence to the electrostatic images during the cascade development process and withstand loss by centrifugal forces operating in magnetic brush development. The carrier may be employed with the toner composition in any suitable combination, generally satisfactory results have been obtained when about 1 part of toner is used with about 5 to about 200 parts by weight of carrier.

The carrier particles may be electrically conductive, insulating, magnetic or non-magnetic (for magnetic brush development they must be magnetic), as long as the carrier particles are capable of triboelectrically obtaining a charge of opposite polarity to that of the toner particles so that the toner particles adhere to and surround the carrier particles.

In developing an electrostatic image to form a positive reproduction of an original, the carrier particle composition and/or toner particle composition is selected so that the toner particles acquire a charge having a polarity opposite to that of the electrostatic latent image so that toner deposition occurs in the charged areas of the masterplate. Alternatively, in reversal reproduction of an electrostatic latent image, the carrier particle composition and toner particle composition is selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic latent image resulting in toner deposition in the non-charged areas of the masterplate.

The invention will now be further illustrated by means of examples.

#### Comparative example 1

A color image was generated using the apparatus shown in figure 1 and described in detail hereinabove, but omitting intermediate sintering of the toner images on the toner image bearing receiver. A polyester (Atlat T500) based toner set was used, having a volume average particle size diameter around 6  $\mu\text{m}$  as determined by Coulter Counter.

Experimentally it was determined that of the total weight of toner deposited on the receiver by transfer in the four toner transfer stations, 3 % was re-transferred to the drum-like members by retro-toner pick-up, in each subsequent transfer step which results in a noticeable loss of optical density on the final receiver. After the fourth transfer step this loss of weight of deposited toner on the receiver increased to 10 % of the toner weight originally deposited to the receiver for the first color.

Moreover, experimentally a loss in transfer efficiency was observed for the second, third and fourth toner layer when underlying previous color layers were present. This resulted in the worst case

to a reduction in transfer efficiency from 95 % to 80 %. An accumulated electrical counter potential of 200 V on three deposited colored toner layers on the receiver was observed. Accordingly a poorer transfer efficiency on said position was observed with respect to "naked" places.

#### Comparative example 2

Example 1 was repeated with the exception that intermediate fusing took place, using heated roller fusing such as described in the section 'final fusing station' herefore and operating at 180 °C for the fuser roller temperature and 120 °C for the pressure roller temperature. The problems described in example 1 were neutralized, however the dimensional stability of the paper (125 g/m<sup>2</sup>) was poor ( $\Delta 1 = 2,5 \text{ mm/m}$ ) resulting in unacceptable registration errors for the full-color images.

#### Comparative example 3

Example 2 was repeated using IR-fusing such as described in EU-A-0 122 650. Same results were obtained as in comparative example 2 and no sufficient difference in heat acceptance between toner and paper was realized.

#### Example 4

Example 2 was repeated with the difference however that a flash fusing system was used, whereby the fusing energy was adapted in accordance with the spectral absorbance of the different colored toners ( $Y > M > C > K$ ) and adjusting its level to realise sintering of the toners deposited to the receiver. Typical values for discharge time were set at 1 msec, and energy densities were for Y : 0.50 J/cm<sup>2</sup>, for M : 0.42 J/cm<sup>2</sup>, for C : 0.35 J/cm<sup>2</sup> and for K : 0.20 J/cm<sup>2</sup>. Sintering was realized as becomes apparent from the fact that the image shows poor rubbing characteristics, and as only partial discharging occurred approximately 50 %. The flashing was realized, providing a cold backing for the receiver containing the toner image. Sufficient difference in energy absorption is present and sufficient heat dissipation, so that no dimensional change for the receiver could be observed : retro-pick up did not occur and over-all transfer efficiency in each transfer station was superior to 95 %.

#### Example 5

Example 4 was repeated with the exception that no heat dissipating backing was used. The receiver showed on set of dimensional instability prohibitive for high quality applications ( $\Delta 1 = 0,3$

mm/m).

# Claims

1. An electrostatographic imaging process wherein a multi color image is formed by the transfer to a receiver of a set of colored toner compositions and fixing of the entire set of colored toner compositions transferred to said receiver characterised in that before said fixing at least once a sintering of (a) transferred colored toner composition(s) to said receiver is executed. 5
2. An electrostatographic imaging process according to claim 1 wherein after each transfer to said receiver of a colored toner composition and before the transfer to said receiver of the subsequent colored toner composition, a sintering of the transferred colored toner composition to said receiver is executed. 10 15 20
3. An electrostatographic imaging process according to claim 1 or 2 that is either a xerocopying or a xeroprinting process. 25
4. An electrostatographic imaging process according to any of the preceding claims, wherein the sintering of the colored toner composition transferred to the receiver is executed by the application of the flash fusing process. 30
5. An electrostatographic imaging process according to claim 4 wherein the fusing energy is adapted in accordance with the spectral absorbance of the different colored toner compositions and its level is adjusted to realise sintering of the toner compositions deposited on the receiver. 35 40
6. An electrostatographic imaging process according to claims 4 or 5, wherein the flash fusing is executed by the application of a Xenon or Krypton flash lamp. 45
7. An electrostatographic imaging process according to claim 4, 5 or 6 wherein during sintering the receiver is guided over a non-heated contacting backing member. 50
8. An electrostatographic imaging process according to any of the preceding claims wherein the fixing of the entire set of colored toner compositions transferred unto the receiver is executed by the heated roller fusing process. 55
9. An electrostatographic imaging process according to any of the preceding claims, wherein the set of colored toner compositions is a set of blue, red and green toner compositions or a set of cyan, magenta and yellow toner compositions.
10. An electrostatographic imaging process according to claim 9, wherein in addition to the cited set of colored toner compositions, a black toner composition is used.
11. An electrostatographic imaging process according to any of the preceding claims wherein the receiver is paper or a thermoplastic sheet material made of e.g. polyethylene terephthalate.
12. An electrostatographic imaging process according to any of the preceding claims wherein the set of colored toner composition is a set of two-component developer compositions comprising colored toner particles.
13. An electrostatographic imaging apparatus wherein a multi color image is formed by the subsequent transfer to a receiver of a set of colored toner compositions and fixing of the entire set of colored toner compositions transferred to said receiver characterised in that before said fixing at least once a sintering of (a) transferred colored toner composition(s) to said receiver is executed.
14. An electrostatographic imaging apparatus according to claim 13 wherein after each transfer to said receiver of a colored toner composition and before the transfer to said receiver of the subsequent colored toner composition, a sintering of the transferred colored toner composition to said receiver is executed.
15. An electrostatographic imaging apparatus according to claim 13 or 14 for the performance of either the xerocopying or xeroprinting process.
16. An electrostatographic apparatus according to claims 13, 14 or 15 wherein the sintering of the colored toner compositions transferred to the receiver is executed by the application of the flash fusing process.
17. An electrostatographic apparatus according to any of claims 13 to 16 wherein the fusing energy is adapted in accordance with the spectral absorbance of the different colored toner compositions and its level is adjusted to realise sintering of the toner compositions deposited on the receiver.

18. An electrostatographic imaging apparatus according to any of claims 16 to 17 wherein the flash fusing is executed by the application of a Xenon or Krypton flash lamp.

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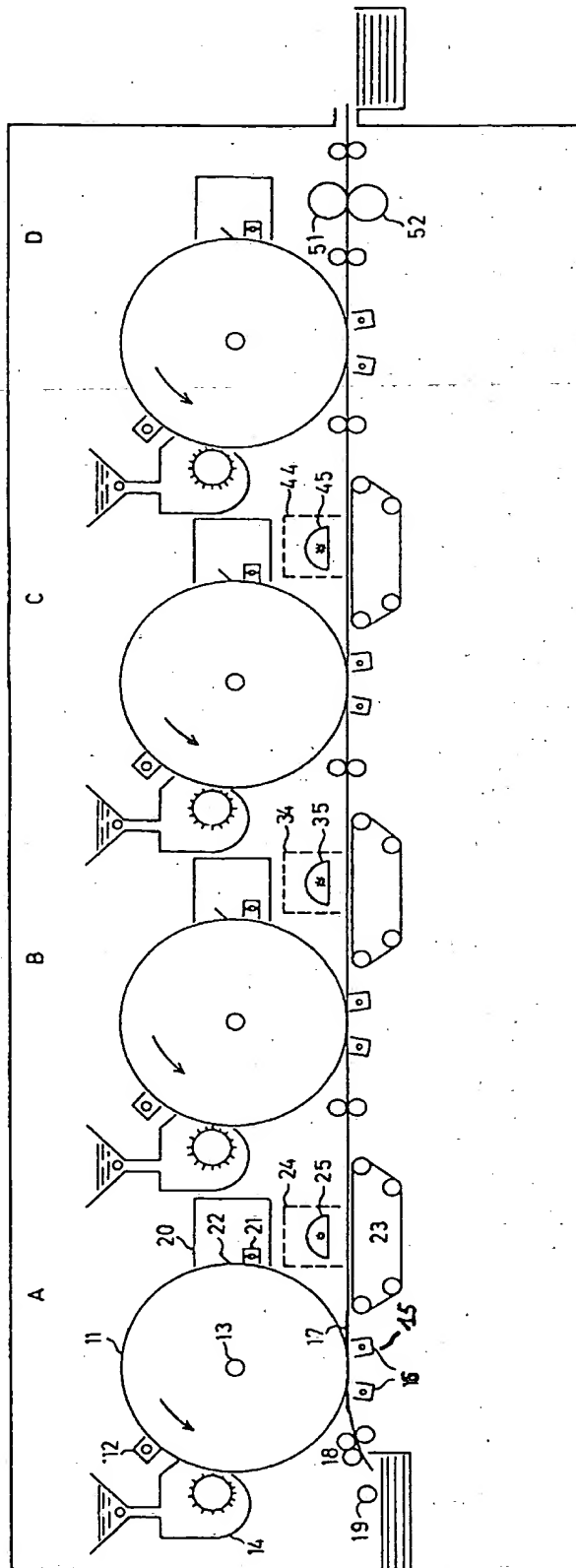
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FIG. 1



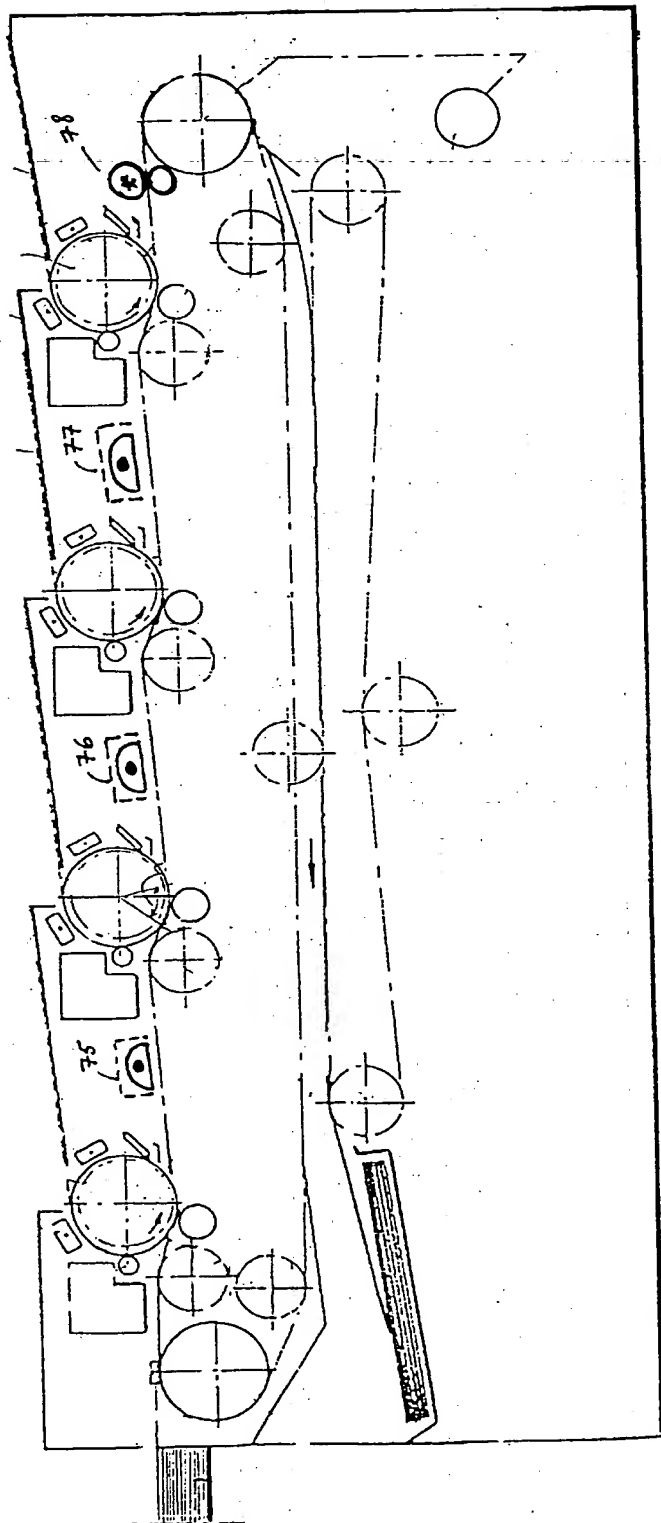
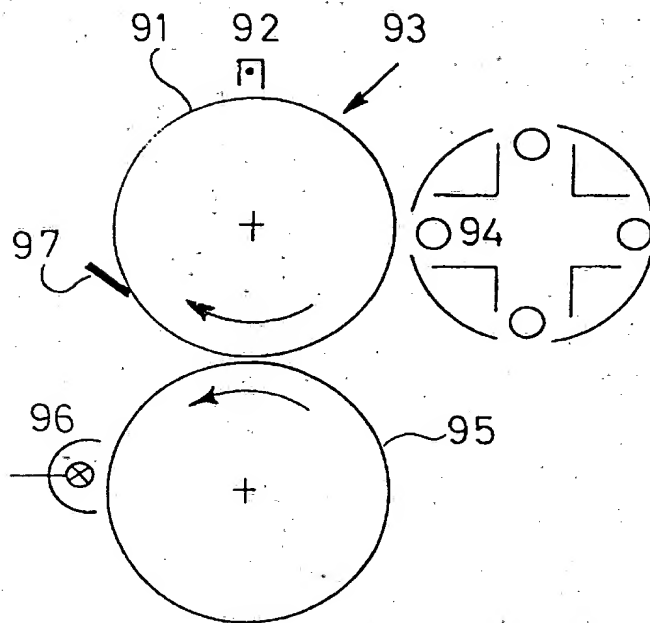
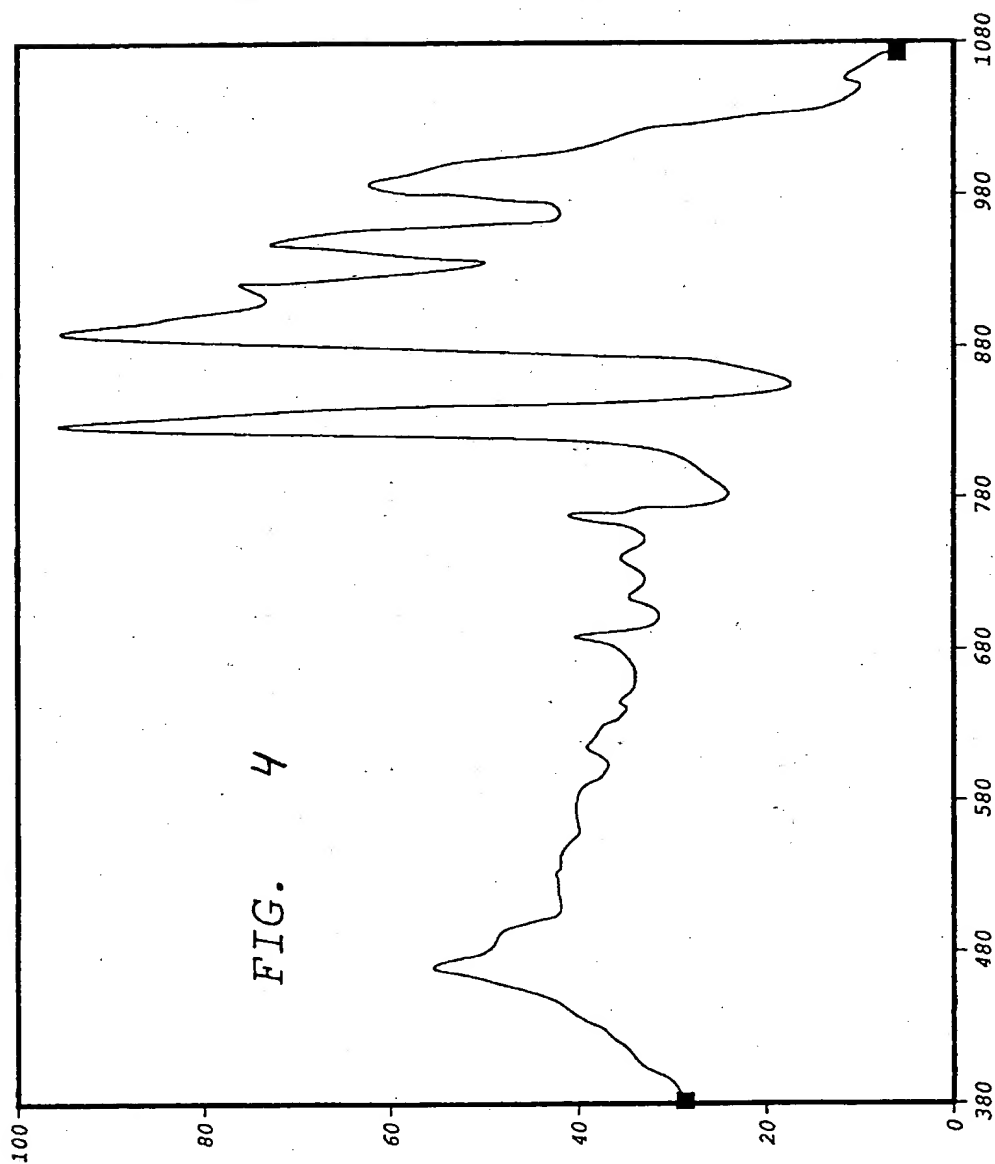


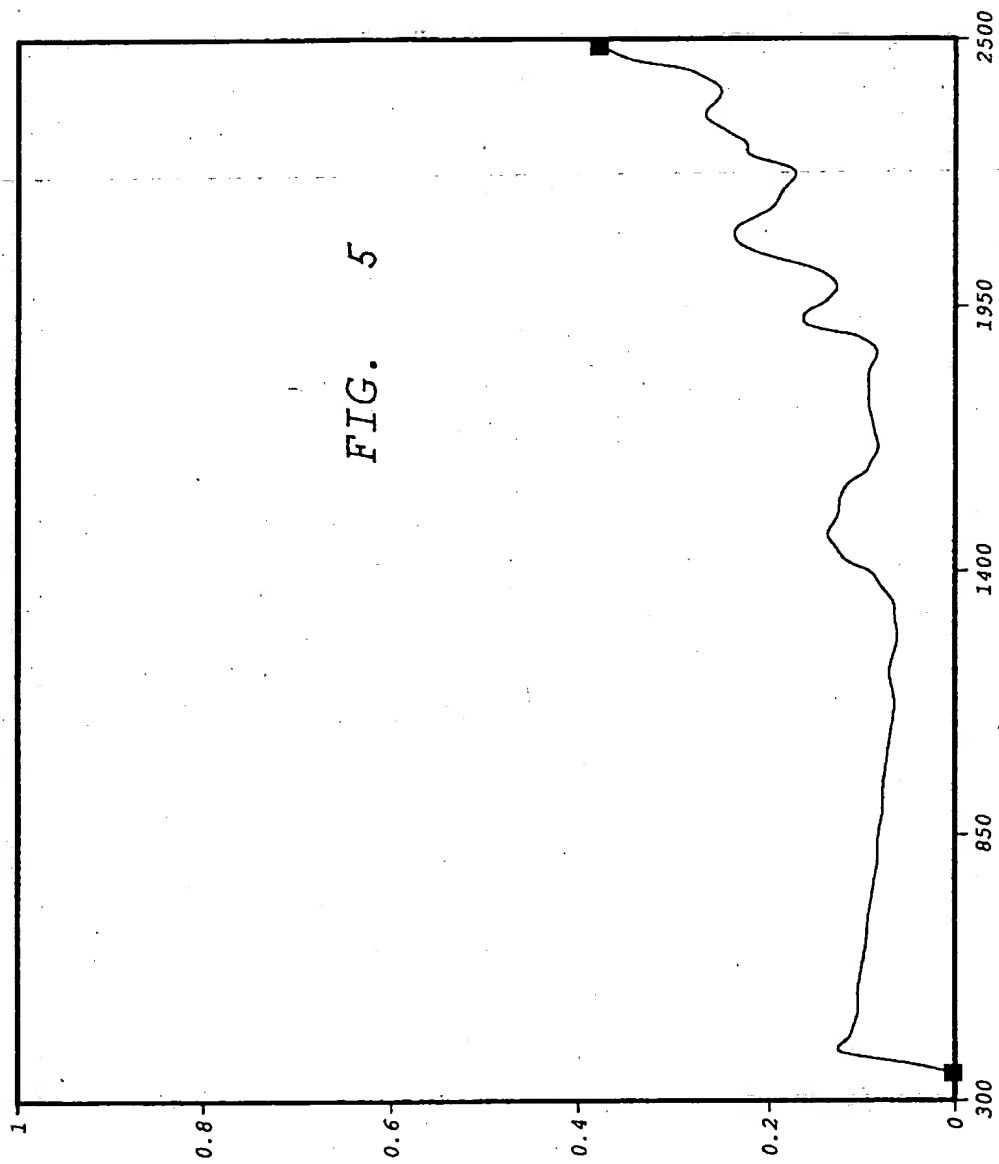
Fig. 2

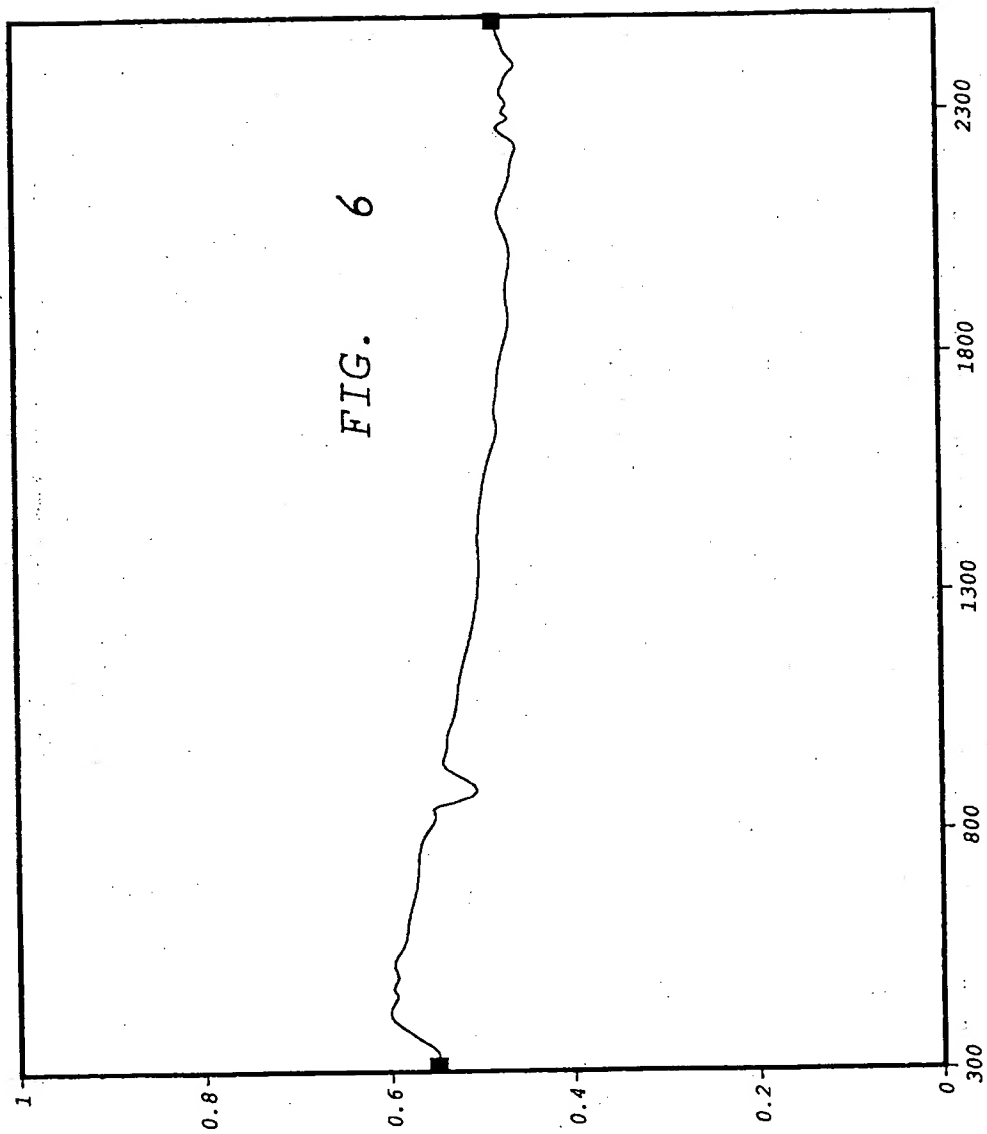
FIG. 3

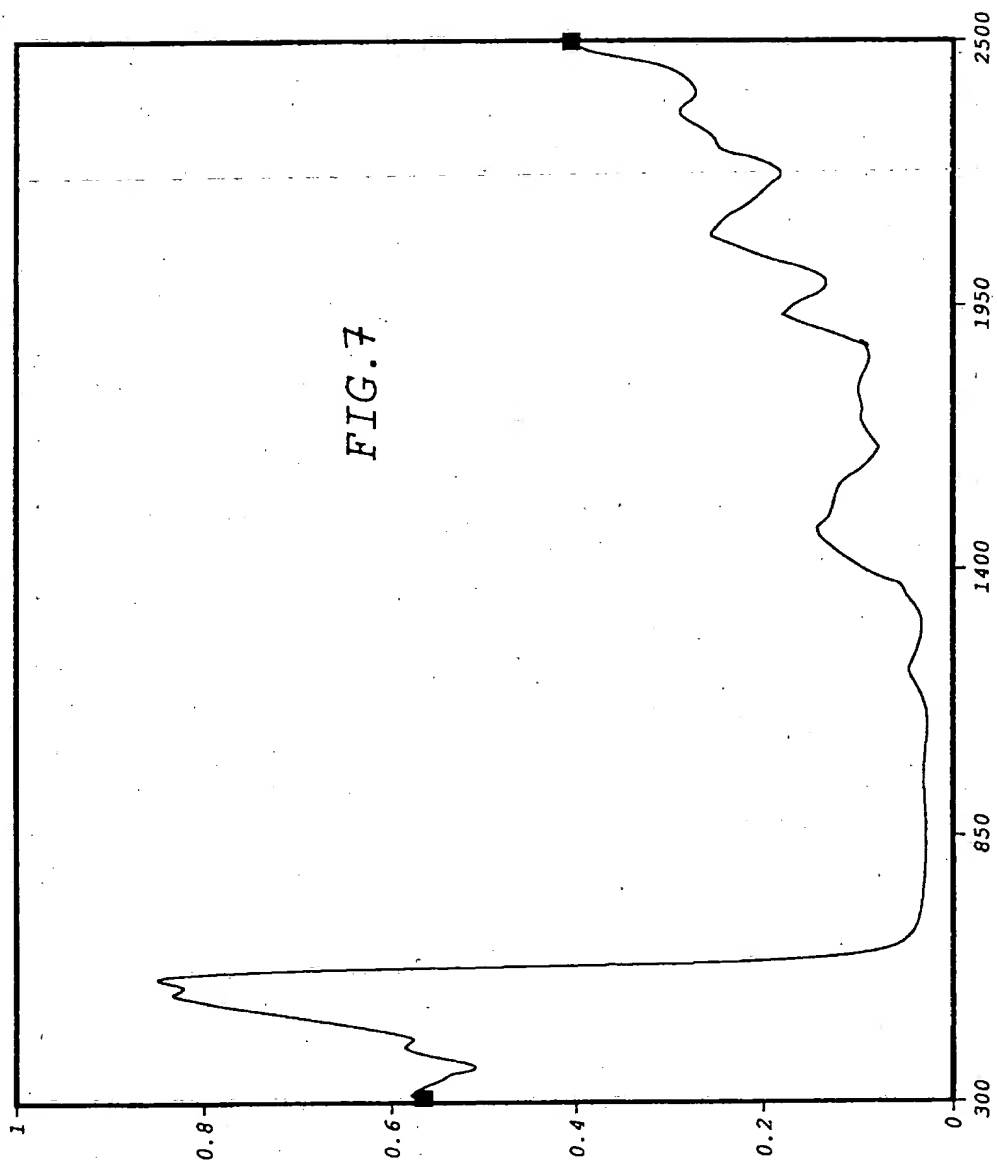


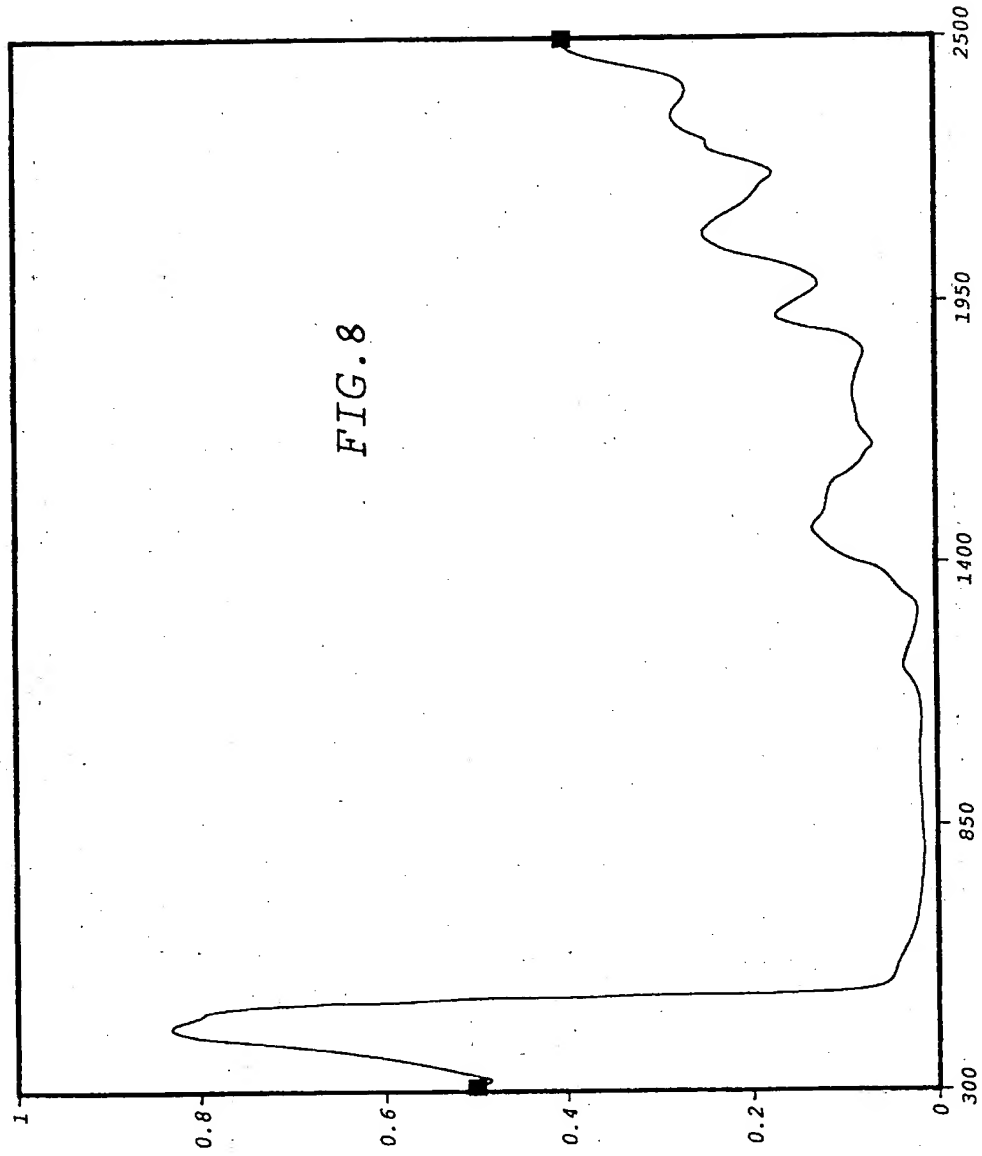


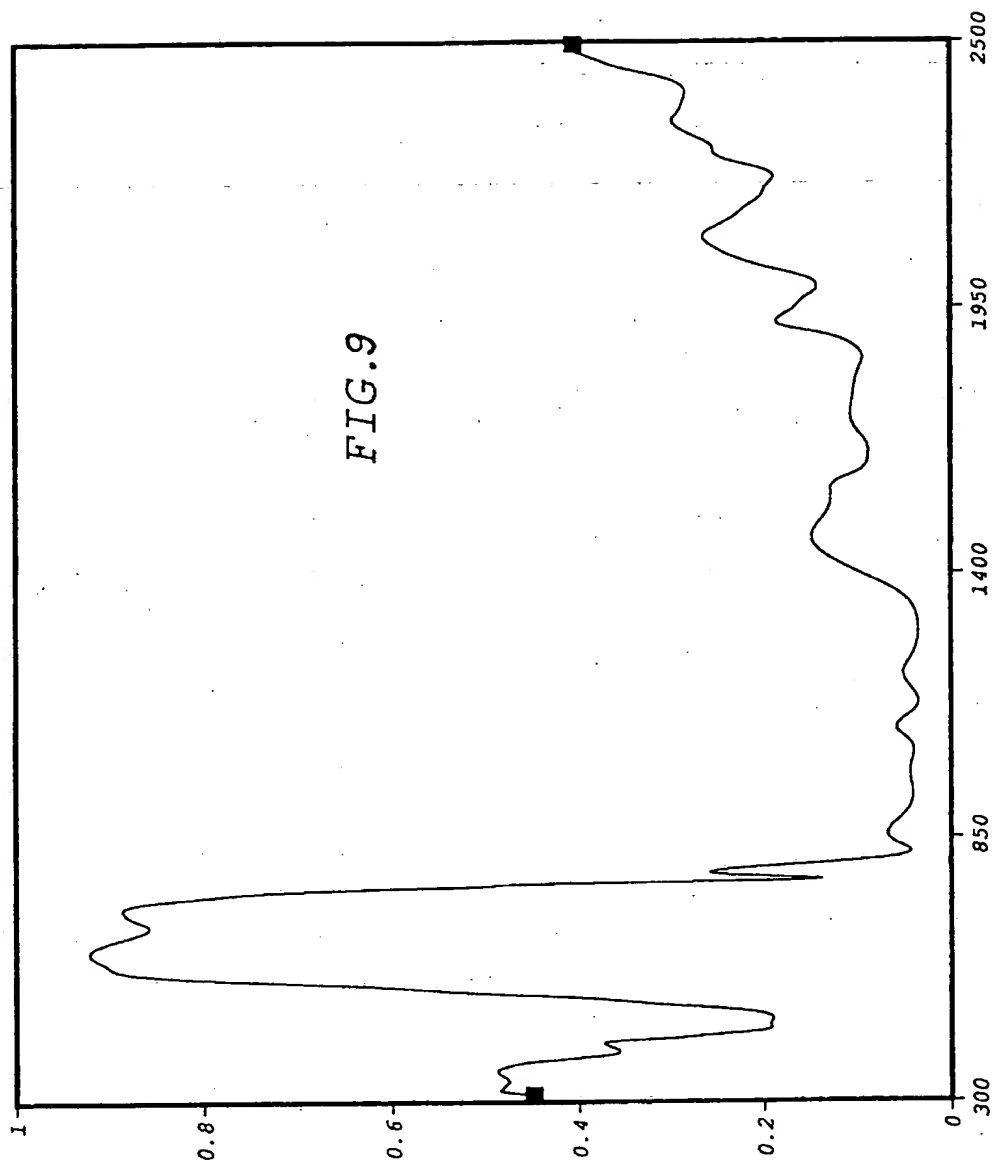














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## EUROPEAN SEARCH REPORT

Application Number

EP 90 20 3346

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 309 588 (TOYO SEIKAN KAISHA LTD) * Abstract; figures 1,2,5,6 *	1-3,7,9 13-15	G 03 G 15/01
X	PATENT ABSTRACTS OF JAPAN, vol. 6, no. 217 (P-152)[1095], 30th October 1982; & JP-A-57 120 956 (TOYO DENKI SEIZO K.K.) 28-07-1982	1-3,11, 13-15	
X	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 271 (P-320)[1708], 12th December 1984; & JP-A-59 137 970 (CANON K.K.) 08-08-1984	1-3,13- 15	
A	US-A-4 286 031 (KUEHNLE et al.) * Column 2, line 58 - column 3, line 60; figure 1 *	1-3,5, 13-17	
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 165 (P-291)[1602], 31st July 1984; & JP-A-59 62 878 (NIPPON DENSHIN DENWA KOSHA) 10-04-1984	1-3,9, 10,13- 15	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	XEROX DISCLOSURE JOURNAL, vol. 5, no. 6, November/December 1980, page 659, Stanford, US; D.G. PARKER: "Common pulsed flash energy in magnetic imaging" * The whole disclosure *	1,4,6, 13,16, 18	G 03 G 15/01 G 03 G 15/20
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29-07-1991	Examiner CIGOJ P.M.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			